

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification:</b> C08F 297/04, C08L 53/02	<b>A1</b>	<b>(11) International Publication Number:</b> WO 94/22931 <b>(43) International Publication Date:</b> 13 October 1994 (13.10.94)
<b>(21) International Application Number:</b> PCT/EP94/00988 <b>(22) International Filing Date:</b> 28 March 1994 (28.03.94) <b>(30) Priority Data:</b> 93200909.5 30 March 1993 (30.03.93) EP (34) Countries for which the regional or international application was filed: GB et al. <b>(71) Applicant:</b> SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). <b>(72) Inventors:</b> VAN WESTRENEN, Jeroen; Badhuisweg 3, NL-1031 CM Amsterdam (NL). VEURINK, Jacqueline, Margaretha; Badhuisweg 3, NL-1031 CM Amsterdam (NL). VAN DONGEN, Arie; Badhuisweg 3, NL-1031 CM Amsterdam (NL). BROEKHUIS, Antonius, Augustinus; Badhuisweg 3, NL-1031 CM Amsterdam (NL).		<b>(81) Designated States:</b> BR, CN, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PROCESS FOR THE PREPARATION OF A BLOCK COPOLYMER COMPOSITION AND BLOCK COPOLYMER COMPOSITION  <b>(57) Abstract</b>  A process is provided for preparing block copolymer compositions, which process comprises the subsequent steps of: (1) polymerizing vinyl aromatic monomer in an inert hydrocarbon solvent in the presence of an organolithium initiator until substantially complete conversion; (2) adding conjugated diene monomer to the polymerization mixture and allowing said conjugated diene monomer to polymerize until substantially complete conversion; (3) adding a second portion of organolithium initiator, followed by the addition of a second portion of conjugated diene monomer and allowing said conjugated diene monomer to polymerize until substantially complete conversion; (4) adding a second portion of vinyl aromatic monomer and allowing said vinyl aromatic monomer to polymerize until substantially complete conversion; and (5) adding a terminating agent. Furthermore, a block copolymer composition is provided comprising: (i) a triblock copolymer A-B-B'-A' having two different or equal polymer endblocks A and A' derived from vinyl aromatic monomer and one polymer midblock B-B' derived from conjugated diene monomer, and (ii) a diblock copolymer B'-A' having one polymer block B' derived from conjugated diene monomer and one polymer block A' derived from vinyl aromatic monomer, wherein the molar weight ration A' (triblock)/A' (diblock) is in the range of from 0.9 to 1.1, wherein both block copolymers are obtained by sequential polymerization and wherein the triblock copolymer as well as the diblock copolymer have a vinyl aromatic content of 55 % by weight or less based on the total weight of the triblock copolymer and diblock copolymer, respectively.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

PROCESS FOR THE PREPARATION OF A BLOCK COPOLYMER COMPOSITION  
AND BLOCK COPOLYMER COMPOSITION

The present invention relates to a process for the preparation of a block copolymer composition and to block copolymer compositions obtainable by this process. More specifically, the present invention relates to a process for the preparation of a  
5 block copolymer composition comprising two linear vinyl aromatic-conjugated diene block copolymers, said process comprising different initiation steps, and to compositions obtainable by this process.

10 From U.S. Patent No. 4,096,203 a process for the preparation of a block copolymer composition for use in adhesive compositions is known, which process involves in the first two steps the preparation of a lithium terminated monoalkenyl arene(A)-conjugated diene(B) diblock copolymer AB-Li by means of solution anionic  
15 polymerization. In the third step the AB-Li diblock copolymer subsequently is reacted with a coupling agent in such amount and under such conditions that the coupling efficiency of the process is varied within the range of from 20 to 80%, thereby controlling the cohesive strength of the adhesive composition wherein the block copolymer composition is to be applied. Said U.S. patent discloses  
20 three possible methods for controlling, i.e. reducing, the coupling efficiency, namely

- (1) underdosing of the coupling agent, i.e. adding less coupling agent than the stoichiometric amount required for complete coupling of the living block copolymers;
- 25 (2) premature addition of terminating agent; and
- (3) performing the coupling reaction at elevated temperatures, so that thermal termination of a part of the living block copolymers occurs.

If the coupling agent is a difunctional coupling agent such as e.g. dibromoethane, it will be appreciated that controlling the coupling efficiency in fact means controlling the ratio between triblock and diblock copolymer in the final block copolymer composition. However, controlling this triblock/diblock copolymer ratio by the above described methods is not very precise and cannot offer the desired optimum flexibility. An important factor in this respect is the fact that every coupling agent has a maximum coupling efficiency lower than 100%. Consequently, it is only possible by any of the methods described above to accomplish a coupling efficiency which is lower than the maximum coupling efficiency of the coupling agent employed. This considerably limits the range within which the triblock/diblock copolymer ratio can vary.

Moreover, commonly applied difunctional coupling agents such as dibromoethane cause the coupled product to have a relatively poor colour stability.

Hence, it is an object of the present invention to provide a process for the preparation of a block copolymer composition comprising a linear vinyl aromatic-conjugated diene triblock copolymer and a vinyl aromatic-conjugated diene diblock copolymer, wherein the weight ratio between triblock and diblock copolymer may have any desired value. It is a further object to provide a process wherein a very effective and high level of controllability of the weight ratio between the tri- and diblock copolymer in the composition on the one hand and their respective molecular weights on the other hand can be achieved in order to obtain tailor made polymer compositions having the desired properties. It is also an object of the present invention to provide a process for preparing a block copolymer composition which has very good colour stability.

Another obvious process for preparing a block copolymer composition comprising a triblock copolymer and a diblock copolymer, both being derived from a vinyl aromatic monomer and a conjugated diene, is physically blending the triblock and diblock copolymer, which have been prepared independently. However such

process would require large blending capacity and therefore is undesired. Moreover, it will be appreciated that the separate preparation of the tri- and diblock copolymer makes it extremely difficult to accomplish that the vinyl aromatic polymer block of the diblock copolymer is substantially identical to one of the terminal vinyl aromatic polymer blocks of the triblock copolymer.

Therefore, beside the fact that the present invention aims to prepare both triblock and diblock copolymer in one process, it is also an object of the present invention to provide a block copolymer composition wherein the vinyl aromatic polymer block of the diblock copolymer is substantially identical to at least one vinyl aromatic endblock of the triblock copolymer.

From U.S. Patent No. 4,335,221 a composition of linear triblock copolymers having a monovinyl aromatic content of 70-80% by weight and a conjugated diene content of 20-30% by weight is known, prepared by a reinitiation process comprising three process stages:

- (1) polymerization of 40 to 80% by weight of the total monovinyl aromatic monomer to be used in an inert solvent in the presence of a monolithium-hydrocarbon initiator until the monomer has been substantially completely converted;
- (2) adding the remaining amount of initiator, adding a further amount of 15 to 30% by weight of monovinyl aromatic monomer to be used and polymerizing until the monomer has been substantially completely converted; and finally
- (3) adding a mixture of all conjugated diene monomer to be used and the remaining amount of monovinyl aromatic monomer and polymerizing until complete conversion of the monomers, followed by the addition of a protonactive compound in order to terminate the polymer chains formed.

As the rate of polymerization of a conjugated diene is in general greater than that of a monovinyl aromatic compound if both are present in one reaction mixture, it will be appreciated that in step (3) a tapered polymer block is formed. As a result, all block

copolymers which are present in the polymer composition have a terminal tapered copolymer block.

European Patent Application No. 0,242,614 discloses a multistage solution polymerization process for producing a mixture of several monovinyl aromatic-conjugated diene block copolymers, each having a terminal tapered copolymer block and a monovinyl aromatic content between 55 and 95% by weight. Said process comprises five subsequent polymerization stages, whereby the polymerization reaction in each stage is allowed to proceed until substantially no free monomer is present anymore. Said five stages are:

- (1) initiator and monovinyl aromatic monomer,
- (2) initiator and monovinyl aromatic monomer,
- (3) conjugated diene monomer,
- (4) initiator and monovinyl aromatic monomer, and
- (5) conjugated diene monomer and monovinyl aromatic monomer.

The polymer blends prepared according to the above described multiple initiation processes are rather hard products due to the relatively high content of monovinyl aromatic compound. Such blends are useful in products requiring good craze-resistance, little colour and a high degree of transparency.

The present invention, however, aims to provide a polymer composition of two linear block copolymers, which is elastic and which can be suitably applied in e.g. adhesive formulations and which can be prepared in one process without needing any blending equipment. It will be appreciated that this is very attractive from an economical point of view. It is a further object of the present invention to provide block copolymers having a narrow molecular weight distribution of the vinyl aromatic polymer blocks. In this connection it is noted that the polymer compositions of the before-mentioned prior art multiple initiation processes are described to have a polymodal molecular weight distribution, whereby the initially formed monovinyl aromatic polymer blocks have different molecular weights due to reinitiation during the formation of said monovinyl aromatic blocks.

All the fore-mentioned objects have been met by the process according to the present invention.

Accordingly, the present invention relates to a process for the preparation of a block copolymer composition, which process comprises the subsequent steps of:

- (1) polymerizing vinyl aromatic monomer in an inert hydrocarbon solvent in the presence of an organolithium initiator until substantially complete conversion;
- (2) adding conjugated diene monomer to the polymerization mixture and allowing said conjugated diene monomer to polymerize until substantially complete conversion;
- (3) adding a second portion of organolithium initiator, directly followed by the addition of a second portion of conjugated diene monomer and allowing said conjugated diene monomer to polymerize until substantially complete conversion;
- (4) adding a second portion of vinyl aromatic monomer and allowing said vinyl aromatic monomer to polymerize until substantially complete conversion; and
- (5) adding a terminating agent.

After the polymerization has been terminated, the obtained product can be isolated, e.g. by steam stripping or flash evaporation.

With the expression "until substantially complete conversion" as used throughout the present specification in connection with the different polymerization reactions involved, is meant that a polymerization is allowed to proceed until at least 90%, preferably at least 95% and most preferably at least 98%, of the initially charged monomer has been polymerized.

It will be appreciated that the process according to the present invention results in a block copolymer composition comprising a triblock copolymer and a diblock copolymer whereby the vinyl aromatic polymer block of the diblock copolymer is substantially identical to the last formed vinyl aromatic polymer block of the triblock copolymer. The term "substantially identical" as used in this connection means that the molar weight ratio

between vinyl aromatic polymer block of the diblock copolymer and the last formed vinyl aromatic polymer block of the triblock copolymer is within the range from 0.9 to 1.1, more suitably 0.95 to 1.05 and most suitably is equal to 1.

5 The above described process may be illustrated by the reaction scheme of Figure 1, wherein  $A_1$  represents a poly(vinyl aromatic) block,  $B_i$  represents a poly(conjugated diene) block and the index number  $i$  indicates the process step in which a polymer block is formed.

10 Step (1):  $A_1-Li$  (first initiation)  
 Step (2):  $A_1-B_2-Li$   
 Step (3):  $A_1-B_2-B_3-Li$  +  $B_3-Li$  (second initiation)  
 Step (4):  $A_1-B_2-B_3-A_4-Li$  +  $B_3-A_4-Li$   
 Step (5):  $A_1-B_2-B_3-A_4$  +  $B_3-A_4$  (termination)

15 Figure 1 Reaction scheme

It will be appreciated that the conjugated diene blocks  $B_2$  and  $B_3$  can be regarded as one conjugated diene polymer block, if they are bonded together to form the polymer unit  $B_2-B_3$ . Consequently, the block copolymer designated as  $A_1-B_2-B_3-A_4$  should be regarded as a triblock copolymer.

20 In a preferred embodiment of the process according to the present invention the amount of conjugated diene added in step (3) is such that the molar weight ratio between the polymer blocks  $B_3$  and  $B_2-B_3$  as expressed in the reaction scheme of figure 1 is in the  
 25 range of from 0.3 to 0.7, more preferably 0.4 to 0.6 and even more preferably 0.45 to 0.55. Most preferably however, said weight ratio is equal to 0.5, which implies that the molar weights of the polymer blocks  $B_2$  and  $B_3$  are identical. In the event said molar weight ratio is 0.5, the total amount of conjugated diene added in  
 30 step (3) must be larger than the amount of conjugated diene added in step (2), as a certain part of the conjugated diene added in step (3) will also form polymer blocks  $B_3$  of the final diblock copolymer  $B_3-A_4$ .

35 It will be appreciated that the process according to the present invention enables the preparation of a block copolymer



composition wherein the vinyl aromatic contents of both triblock and diblock copolymer are either the same or different. It is preferred that they are the same.

In principle, any desired weight ratio between tri- and diblock copolymer can be accomplished by the process according to the present invention. It is however preferred that this ratio lies within the range of from 0.01 to 100, preferably 0.1 to 50 and even more preferably 0.2 to 20.

The vinyl aromatic monomer may be selected from styrene,  $\alpha$ -methylstyrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 1,3-dimethylstyrene or mixtures thereof, of which styrene is the most preferred.

The conjugated diene monomer may be any conjugated diene containing from 4 to 8 carbon atoms, such as 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene or mixtures thereof, of which 1,3-butadiene, isoprene or mixtures thereof are preferred. Isoprene is the most preferred monomer, in particular for application in adhesive formulations.

It will be appreciated that in the reaction scheme of figure 1  $B_2$  and  $B_3$  may be derived from either the same conjugated diene or different conjugated dienes. Accordingly, when S and S' represent polystyrene blocks, I and I' represent polyisoprene blocks and Bu and Bu' represent polybutadiene blocks, the following compositions of tri- and diblock copolymer are possible:

S-I-I'-S'/I'-S'	S-Bu-Bu'-S'/Bu'-S'
S-I-Bu'-S'/Bu'-S'	S-Bu-I'-S'/I'-S'

Also included are the compositions comprising a tri- and a diblock copolymer, wherein  $B_2$  and/or  $B_3$  are random or tapered copolymer blocks derived from different conjugated diene monomers.

For instance,  $B_2$  and/or  $B_3$  may be derived from randomly copolymerized butadiene and isoprene. Alternatively, the blocks  $B_2$  and  $B_3$  may represent polybutadiene blocks having different degrees of 1,2-polymerization (1,2-vinyl contents). Block  $B_2$  may e.g. have a low 1,2-vinyl content, while block  $B_3$  has a high 1,2-vinyl

content. This can be achieved by adding a structure modifier together with the second portion of organolithium initiator. It is however preferred that the blocks  $B_2$  and  $B_3$  are both homopolymer blocks derived from the same conjugated diene.

5       The inert hydrocarbon solvent may be any solvent known in the art to be suitably applied as a polymerization solvent. Examples of suitable inert hydrocarbon solvents are cyclic aliphatic hydrocarbons such as cyclohexane and cyclopentane, and mixtures thereof with linear or branched aliphatic hydrocarbons such as  
10   n-hexane and isopentane. Particularly suitable are cyclohexane, cyclohexane/n-hexane mixtures, cyclohexane/isopentane/n-hexane mixtures, cyclopentane and cyclopentane/isopentane mixtures.

Cyclohexane/isopentane/n-hexane mixtures, cyclohexane and cyclopentane are preferred.

15       The organolithium initiator may be any organic lithium compound which is commonly known to act as an initiator in polymerization reactions. A preferred class of organolithium compound are alkyl lithium compounds, wherein the alkyl group may be a linear alkyl group or a cycloalkyl group. Preferred alkyl  
20   lithium compounds are n-butyl lithium and sec-butyl lithium, with sec-butyl lithium being most preferred.

As the terminating agent commonly known active hydrogen compounds such as water, alcohols, phenols and carboxylic acids may be used. In this case alcohols are preferred, of which methanol and  
25   ethanol are most preferred.

If butadiene is used as the conjugated diene monomer, small amounts of structure modifiers, such as ethers and tertiary amines, may be present in the reaction mixture for regulating the degree of 1,2-polymerization. Such structure modifiers may be either present  
30   during the whole polymerization process or during only a part thereof, most suitably the second part, i.e. after reinitiation.

The polymerization reactions at the different stages of the process may be carried out at equal or different temperatures within the range of from  $-10\text{ }^{\circ}\text{C}$  to  $150\text{ }^{\circ}\text{C}$ , preferably  $10\text{ }^{\circ}\text{C}$  to

100 °C. The reaction pressure is not bound to any particular value, but should only be sufficient to maintain the reaction mixture in the liquid phase.

The present invention also relates to a block copolymer composition comprising:

- (i) a triblock copolymer A-B-B'-A' having two different or equal polymer endblocks A and A' derived from vinyl aromatic monomer and one polymer midblock B-B' derived from conjugated diene monomer, and
- (ii) a diblock copolymer B'-A' having one polymer block B' derived from conjugated diene monomer and one polymer block A' derived from vinyl aromatic monomer,

wherein the molar weight ratio A'(triblock)/A'(diblock) is in the range of from 0.9 to 1.1, wherein both block copolymers are obtained by sequential polymerization and wherein the triblock copolymer as well as the diblock copolymer have a vinyl aromatic content of 55% by weight or less based on the total weight of the triblock copolymer and diblock copolymer, respectively.

It is preferred that the vinyl aromatic polymer block of the diblock copolymer is substantially identical to at least one of the vinyl aromatic polymer blocks of the triblock copolymer. In other words, the molar weight ratio A'(triblock)/A'(diblock) preferably is in the range of from 0.95 to 1.05 and most preferably is equal to 1.

It is preferred that the molar weight ratio B'/B-B' is in the range of from 0.3 to 0.7, preferably 0.45 to 0.55 and most preferably is equal to 0.5.

In principle, the weight ratio between triblock and diblock copolymer is not bound to any particular value. It is however preferred that this ratio lies within the range of from 0.01 to 100, preferably 0.1 to 50 and even more preferably 0.2 to 20.

With the term "apparent molecular weight" as used throughout this specification, the molecular weight of a polymer, except polystyrene itself, as measured with gel permeation chromatography (GPC) using polystyrene calibration standards is meant.

The vinyl aromatic contents of the tri- and diblock copolymer may vary over a wide range. However, as the block copolymer composition according to the invention is most suitably applied in adhesive formulations, the vinyl aromatic content should not be too high, i.e. should not exceed 55% by weight based on the total weight of block copolymer. More particularly, the vinyl aromatic content of both tri- and diblock copolymer is preferably in the range of from 10 to 50% by weight, more preferably in the range of from 12 to 40% by weight and most preferably in the range of from 14 to 35 % by weight. The vinyl aromatic contents of both triblock and diblock copolymer may be the same or different, but it is preferred that they are the same.

The molecular weight of the vinyl aromatic polymer blocks is not bound to specific values, but may suitably be within the range of from 5,000 to 30,000, preferably 8,000 to 20,000. The apparent molecular weight of the triblock copolymer may suitably be in the range of from 50,000 to 400,000, preferably 80,000 to 250,000.

The most preferred vinyl aromatic monomer is styrene, while the conjugated diene monomer preferably is selected from butadiene, isoprene and mixtures thereof with isoprene being most preferred.

The invention is further illustrated by the following examples without restricting the scope of the invention to these particular embodiments. In these examples the molecular weight of the block copolymers prepared is determined by Gel Permeation Chromatography (GPC) using polystyrene calibration standards as described in ASTM D 3536. The polystyrene content of the block copolymers is determined according to the method described in ASTM D 3314. From the data obtained by these methods other data such as the the molar weight ratio I'/II' and the styrene weight ratio triblock/diblock are derived.

#### Example 1

A block copolymer composition comprising a styrene-isoprene-styrene triblock copolymer (SII'S') and a styrene-isoprene diblock copolymer (S'I'), wherein:

- (a) both block copolymers had a target styrene content of 15% by weight; and  
 (b) the target weight ratio triblock/diblock was 85/15;  
 was prepared as follows.

- 5 Step (1): 38 g of styrene was added to 4675 g of cyclohexane at 50 °C, after which 3.55 mmol of sec-butyl lithium (s-BuLi) was added. The polymerization was complete after 38 minutes (99% conversion).  
 10 Step (2): The temperature was raised to 60 °C and 215 g of isoprene was added. The polymerization was allowed to proceed 24 minutes (99% conversion).  
 Step (3): A second portion of s-BuLi (1.25 mmol) was added, followed by 291 g of isoprene. The polymerization was allowed to proceed for 25 minutes (99% conversion).  
 15 Step (4): A final portion of 51 g of styrene was added and polymerization was allowed to proceed for 17 minutes (99% conversion).  
 Step (5): 5.35 mmol of ethanol was added as a terminating agent to quench the styrenyl anion.

20 The product was isolated by steam stripping to give white crumbs.

Analysis with GPC revealed the following results as to the (apparent) molecular weight of the different polymer blocks:

	Step (1) :	MW	S	10700	[—]
25	Step (2) :	MW	SI	110300	[—]-----
	Step (3) :	MW	SII'	214900	[—]-----
		MW	I'	109800	-----
	Step (4) :	MW	SII'S'	224800	[—]-----[—]
		MW	I'S'	119190	-----[—]

30 Further analysis of the block copolymer composition showed that the styrene content of both triblock and diblock copolymer was 15% by weight, that both S' blocks of the triblock and diblock copolymer were identical, that the molar weight ratio I'/II' was 0.5 and that the styrene weight ratio triblock/diblock was 85/15.

Example 2

A block copolymer composition comprising a styrene-butadiene-styrene triblock copolymer (SBB'S') and a styrene-butadiene diblock copolymer (S'B'), wherein:

- 5 (a) both block copolymers had a target styrene content of 15% by weight; and
- (b) the target weight ratio triblock/diblock was 85/15; and was prepared in a similar way as described in Example 1, using the following amounts of monomer and initiator:

- 10 Step (1) : 75 g styrene and 4.84 mmol s-BuLi  
Step (2) : 175 g butadiene  
Step (3) : 1.68 mmol s-BuLi and 237 g butadiene  
Step (4) : 101 g styrene

Analysis with GPC revealed the following results as to the (apparent) molecular weight of the different polymer blocks:

S	:	15496			
SB	:	83050			
SBB'	:	151000	B'	:	71800
SBB'S'	:	165500	B'S'	:	85790

20 Further analysis of these results showed that the styrene content of both triblock and diblock copolymer was 15% by weight, that both S' blocks of the triblock and diblock copolymer were identical, that the molar weight ratio B'/BB' was 0.5 and that the styrene weight ratio triblock/diblock was 85/15.

25 Example 3

A block copolymer composition comprising a styrene-butadiene-styrene triblock copolymer (SBB'S') and a styrene-butadiene diblock copolymer (S'B'), wherein:

- 30 (a) the triblock copolymer had a target styrene content of 25% by weight;
- (b) the diblock copolymer had a target styrene content of 40% by weight; and
- (c) the target weight ratio triblock/diblock was 70/30

was prepared in a similar way as described in Example 1, using the following amounts of monomer and initiator:

Step (1) : 75 g styrene and 4.84 mmol s-BuLi

Step (2) : 337 g butadiene

5 Step (3) : 6.636 mmol s-BuLi and 267 g butadiene

Step (4) : 178 g styrene

Analysis with GPC revealed the following results as to the (apparent) molecular weight of the different polymer blocks:

10	S	:	15600		
	SB	:	145600		
	SBB'	:	201000	B'	: 51500
	SBB'S'	:	214150	B'S'	: 65510

15 Further analysis of these results showed that the styrene content of the triblock copolymer was 25% by weight, that the styrene content of the diblock copolymer was 40% by weight, that both S' blocks of the triblock and diblock copolymer were identical, that the molar weight ratio B'/BB' was 0.37 and that the styrene weight ratio triblock/diblock was 60/40.

C L A I M S

1. Process for the preparation of a block copolymer composition, which process comprises the subsequent steps of:

- 5 (1) polymerizing vinyl aromatic monomer in an inert hydrocarbon solvent in the presence of an organolithium initiator until substantially complete conversion;
  - (2) adding conjugated diene monomer to the polymerization mixture and allowing said conjugated diene monomer to polymerize until substantially complete conversion;
  - 10 (3) adding a second portion of organolithium initiator, followed by the addition of a second portion of conjugated diene monomer and allowing said conjugated diene monomer to polymerize until substantially complete conversion;
  - (4) adding a second portion of vinyl aromatic monomer and allowing said vinyl aromatic monomer to polymerize until substantially  
15 complete conversion; and
  - (5) adding a terminating agent.
2. Process according to claim 1, wherein the amount of conjugated diene added in step (3) is such that the molar weight ratio between the conjugated diene polymer blocks of the diblock copolymer and  
20 the triblock copolymer is in the range of from 0.3 to 0.7.
3. Process according to claim 2, wherein the amount of conjugated diene added in step (3) is such that the molar weight ratio between the conjugated diene polymer blocks of the diblock copolymer and the triblock copolymer is 0.5.
- 25 4. Process according to any one of claims 1 to 3, wherein the vinyl aromatic monomer is styrene.
5. Process according to any one of claims 1 to 4, wherein the conjugated diene monomer is selected from butadiene, isoprene and mixtures thereof.
- 30 6. Process according to claim 5, wherein the conjugated diene monomer is isoprene.



7. Process according to any one of claims 1 to 6, wherein the inert hydrocarbon is selected from cyclohexane/n-hexane/isopentane mixtures, cyclohexane and cyclopentane.
8. A block copolymer composition comprising:
- 5 (i) a triblock copolymer A-B-B'-A' having two different or equal polymer endblocks A and A' derived from vinyl aromatic monomer and one polymer midblock B-B' derived from conjugated diene monomer, and
- 10 (ii) a diblock copolymer B'-A' having one polymer block B' derived from conjugated diene monomer and one polymer block A' derived from vinyl aromatic monomer,
- wherein the molar weight ratio A'(triblock)/A'(diblock) is in the range of from 0.9 to 1.1, wherein both block copolymers are obtained by sequential polymerization and wherein the triblock
- 15 copolymer as well as the diblock copolymer have a vinyl aromatic content of 55% by weight or less based on the total weight of the triblock copolymer and diblock copolymer, respectively.
9. Block copolymer composition according to claim 8, wherein the molar weight ratio A'(triblock)/A'(diblock) is equal to 1.
- 20 10. Block copolymer composition according to claim 8 or 9, wherein the molar weight ratio B'/B-B' is in the range of from 0.3 to 0.7.
11. Block copolymer composition according to claim 10, wherein the molar weight ratio B'/B-B' is 0.5.
12. Block copolymer composition according to any one of claims 8
- 25 to 11, wherein the vinyl aromatic contents of the triblock copolymer and the diblock copolymer are in the range of from 14 to 35% by weight.
13. Block copolymer composition according to any one of claims 8 to 12, wherein the triblock copolymer and the diblock copolymer
- 30 have the same vinyl aromatic content.
14. Block copolymer composition according to any one of claims 8 to 13, wherein the weight ratio between triblock copolymer and diblock copolymer lies within the range of from 0.2 to 20.
15. Block copolymer composition according to any one of claims 8
- 35 to 14, wherein the vinyl aromatic monomer is styrene.

16. Block copolymer composition according to any one of claims 8 to 15, wherein the conjugated diene monomer is selected from butadiene, isoprene and mixtures thereof.

5 17. Block copolymer composition according to claim 16, wherein the conjugated diene is isoprene.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08F C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 8723, Derwent Publications Ltd., London, GB; AN 87-159661 HOSHI SUSUMU ET AL. 'block copolymer compsn.' & JP,A,61 254 650 (ASAHI CHEMICAL IND.) 12 November 1986	1-7
Y	see abstract	1-17
X	EP,A,0 330 764 (SHELL INTERNATIONALE RESEARCH) 6 September 1989	8,9, 12-17
Y	see claim 1; examples	1-17
Y	US,A,4 096 203 (SHELL OIL) 20 June 1978 cited in the application see claim 1	1-17

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

29 July 1994

Date of mailing of the international search report

30. 08. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Loiselet-Taisne, S

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0330764	06-09-89	AU-B- 612142	04-07-91
		AU-A- 1484988	22-09-89
		WO-A- 8908128	08-09-89
		US-A- 5089550	18-02-92
-----			
US-A-4096203	20-06-78	NONE	
-----			